

ADDITION REACTIONS OF SOME SUBSTITUTED
p-QUINONEDIBENZENESULFONIMIDES

BY

THOMAS EDWIN YOUNG

B.S., Lehigh University, 1949

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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ACKNOWLEDGMENT

The author wishes to offer his sincere thanks to Dr. Roger Adams, who conceived and supervised this problem, for the opportunity of working in the field of quinone chemistry, and for the frequent advice and encouragement given throughout the course of the investigation.

The author also expresses his appreciation to the Standard Oil Company of California, for Research Fellowships, and to the University of Illinois for a University Fellowship. He is also indebted to Mrs. Elizabeth Leighly and Miss Helen Miklas for the determination and interpretation of infrared absorption spectra, and to Miss Emily Davis, Mrs. Esther Fett, Mrs. Jean Fortney, Mrs. Katherine Pih, and Mr. Joseph Nemeth for the microanalyses.



ADDITION REACTIONS OF SOME SUBSTITUTED *p*-QUINONEDIBENZENESULFONIMIDES

The known modifications of a single substituent on the quinonoid ring of *p*-quinonedibenzenesulfonimide have, thus far, included chloro, methyl, phenylmercapto, aryl, and acetoxy groups (1). The principle objective of the present investigation was to examine further variations in this ring substituent and to determine the orienting effect of such functional groups during conjugate addition reactions of the quinonoid system.

A subsidiary objective, which arose during the course of this work, was to determine a consistently reproducible procedure for the addition of thiols to *p*-quinonedibenzenesulfonimide.

DISCUSSION OF RESULTS

Benzenesulfonation of methoxy-*p*-phenylenediamine led to 2-methoxy-*p*-phenylenedibenzenesulfonamide, which was easily oxidized by lead tetraacetate to 2-methoxy-*p*-quinonedibenzene-sulfonimide. This quinone diimide was stable for only two weeks under ordinary conditions of storage; it reacted readily with hydrogen chloride, thiophenol, and benzenesulfinic acid to form, respectively, 2-methoxy-5-chloro-, 2-methoxy-5-phenylmercapto-, and 2-methoxy-5-benzenesulfonyl-*p*-phenylene-dibenzenesulfonamides. The structures of these adducts were proved by unequivocal syntheses. Oxidation of these 2-methoxy-5-substituted diamides by lead tetraacetate produced the corresponding quinone diimides. 2-Methoxy-5-chloro-*p*-quinonedibenzenesulfonimide added hydrogen chloride to give a mixture of isomeric 2-methoxy-5,x-dichloro-*p*-phenylene-dibenzenesulfonamides. This mixture was not separated but directly oxidized by lead tetraacetate to a mixture of the methoxydichloroquinone diimides, which was extensively reduced on treatment with dry hydrogen chloride.

Both the addition of benzenesulfinic acid to *p*-quinonedibenzesulfonimide and the oxidation of 2-phenylmercapto-*p*-phenylenedibenzesulfonamide with hydrogen peroxide led to 2-benzenesulfonyl-*p*-phenylenedibenzesulfonamide. This product was oxidized by lead tetraacetate to the corresponding quinone diimide in excellent yield. 2-Benzenesulfonyl-*p*-quinonedibenzesulfonimide underwent addition reactions with acetic acid, hydrogen chloride, and benzenesulfinic acid to give 2-benzenesulfonyl-X-acetoxy-, 2-benzenesulfonyl-X-chloro-, and 2,X-bis(benzenesulfonyl)-*p*-phenylenedibenzesulfonamides, in which the X-position was undetermined.

2-Chloro-*p*-quinonedibenzesulfonimide also reacted with benzenesulfinic acid to yield 2-benzenesulfonyl-5-chloro-, and 2-benzenesulfonyl-Z-chloro-*p*-phenylenedibenzesulfonamides. These products both differed from the 2,X-isomer mentioned in the preceding paragraph. While the structure of the 2,5-compound was verified by unequivocal synthesis, the structures of the 2,Z- and 2,X-isomers remained unestablished.

2-Phenylmercapto-*p*-quinonedibenzesulfonimide added thiophenol and benzenesulfinic acid to give 2,Y-bis(phenylmercapto)-, and 2-benzenesulfonyl-Y-phenylmercapto-*p*-phenylenedibenzesulfonamides. Oxidation of either of these adducts with hydrogen peroxide gave the same 2,Y-bis(benzenesulfonyl)-*p*-phenylenedibenzesulfonamide, showing that the orientation of the thiol and sulfinic acid adducts is the same. The absolute determination of the Y-position was not achieved, however, the 2,Y-bis(benzenesulfonyl) diamide proved to be different from the 2,X-isomer obtained previously by the addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-quinonedibenzesulfonimide.

The reaction of thiophenol with 2-methyl-*p*-quinonedibenzesulfonimide in the presence of triethylamine gave an excellent yield of a single 2-methyl-Y-phenylmercapto-*p*-phenylenedibenzesulfonamide, which on oxidation with hydrogen peroxide produced a 2-methyl-Y-benzenesulfonyl-*p*-phenylenedibenzesulfonamide identical with that obtained by addition

of benzenesulfinic acid to the methylquinone diimide.

The reaction of 1-chloro-2-cyano-4-nitrobenzene with the sodium salt of benzenesulfonamide in dimethylformamide gave mediocre yields of 1-benzenesulfonamido-2-cyano-4-nitrobenzene; reduction of the nitro group and benzenesulfonation of the amine produced 2-cyano-*p*-phenylenedibenzenesulfonamide. This compound was oxidized by lead tetraacetate to the quinone diimide, which, though not isolated, reacted *in situ* with hydrogen chloride to yield 2-cyano-X-chloro-*p*-phenylenedibenzenesulfonamide, in which X was not determined.

Catalytic reduction of methyl 5-nitroanthranilate to the corresponding diamine and benzenesulfonation of this product provided 2-carbomethoxy-*p*-phenylenedibenzenesulfonamide, which was oxidized by lead tetraacetate to a bright yellow quinone diimide. The electronically similar 2-nitro-*p*-phenylenedibenzenesulfonamide also reduced lead tetraacetate but no corresponding quinone diimide could be isolated.

A reinvestigation of the previously reported (2) addition of thiols to *p*-quinonedibenzenesulfonimide showed that the trace-presence of an acidic reagent such as sulfuric acid or dioxane-sulfuric acid complex served to inhibit the reduction of the quinone diimide by the mercaptan and permit an addition reaction to predominate. Triethylamine was found to be a generally applicable and superior catalyst for these thiol additions.

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VITA

Thomas Edwin Young was born on September 7, 1924, in Manheim, Pennsylvania. He graduated from Manheim High School in 1941 and entered the United States Army in 1943. After returning from the European Theater, he was married to Hilda Jean Derstler of Manheim, Pennsylvania, in July, 1945. Upon discharge from the Army in 1946, he entered Lehigh University to major in chemical engineering, and in February, 1947, became the father of a son, Robert Edwin. In February, 1949, he received the degree of Bachelor of Science, with honors, from Lehigh University, where he remained as a one-third time graduate assistant until receipt of his Master of Science degree in June, 1950. In the following September, he entered the Graduate College of the University of Illinois, where he held a Standard Oil of California Research Fellowship from September, 1950, to June, 1952, and a University Fellowship from June through August, 1952.

